Epitaxial Growth of $La_{1/3}Sr_{2/3}FeO_3$ thin films by laser ablation

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Abstract

We report on the synthesis of high quality $La_{1/3}Sr_{2/3}FeO_3$ (LSFO) thin films using the pulsed laser deposition technique on both $SrTiO_3$ (STO) and $LaAlO_3$ (LAO) substrates (100)-oriented. From X-Ray diffraction (XRD) studies, we find that the films have an out-of-plane lattice parameter around 0.3865nm, almost independent of the substrate (i.e. the nature of the strains). The transport properties reveal that, while LSFO films deposited on STO exhibit an anomaly in the resistivity vs temperature at $180K$ (corresponding to the charge-ordered transition and associated with a transition from a paramagnetic to an antiferromagnetic state), the films grown on LAO display a very small magnetoresistance behavior and present an hysteresis around $270K$ under the application of a $4T$ magnetic field. The changes in transport properties between both substrates are discussed and compared with the corresponding single crystals.

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The transition metal oxides (TMO) have been extensively studied in the past years, in particular due to the metal-insulator (MI) transition[1]. Among the different compounds, the manganites $RE_{1-x}A_xMnO_3$ (RE=rare earths, A=alkaline earths) have received a great interest these last years due to their colossal magnetoresistance (MR) properties[2,3]. An interesting feature of these materials is the charge-ordering phenomena[4,5] i.e. the ordering of cations of different charges (Mn^{3+}/Mn^{4+} for example) on specific lattice sites. This characteristic can be seen in others compounds such as nickelates[6] or layered manganites[7]. In fact, it has also been recently observed in others perovskites such as $La_{1/3}Sr_{2/3}MnO_3$ (LSFO)[8], which has been first studied by Waugh *et al.*[9]. Even if more studies appear very recently on such materials[10–13], there are vey few reports on thin films growth and to our knowledge, only for the particular composition $SrFeO_{3-\delta}$[12,13]. Interestingly, theses materials show properties close to the manganites and charge disproportionation has also been investigated in the past[14]. Moreover, they are suitable candidates for MR properties[15]. The synthesis of charge-ordered (CO) manganite thin films is difficult owing to the distortion of the lattice induce by the substrate[16] and usually, the properties of the CO thin films are different from the bulk. For example, in the case of $Pr_{0.5}Ca_{0.5}MnO_3$, the CO state can not been completely established. This means that the CO state is weaken due to the substrate-induce strains because it is impossible to accomodate the quite large changes of structural parameters when occuring below the CO transition (T_{CO})[17].

In an effort of understanding the particular substrate-effects of the CO oxide compounds, it is interesting to look at others compositions. $La_{1/3}Sr_{2/3}FeO_3$ is such an example. For these reasons, we have synthesized $La_{1/3}Sr_{2/3}FeO_3$ thin films on two types of substrates that induce compression or tensile strains. We measured the structural lattice parameters and transport properties of the films. Our results are report in this communication.

Thin films of LSFO were grown using the pulsed laser deposition technique. The target used has a nominal composition of $La_{1/3}Sr_{2/3}FeO_3$. In the bulk form, LSFO has a rhombohedral structure ($R\overline{3}c$) with a lattice constant $a_R = 0.547nm$ and an edge angle $a_R = 60.1°$ at room temperature[11,14]. In fact, the average structure can be considered as a cubic per-

ovskite slightly distorted with a parameter close to $a \approx 2a_P \approx 2 \times 0.387nm = 0.774nm$ (where a_P being the ideal parameter of the cubic perovskite). Thus, we expect to be able to grow a thin film of this composition directly on a perovskite substrate. For facilitating the reading of this paper, we keep the simple cubic cell notation (index with C). Substrates used were (100)-$SrTiO_3$ (STO, cubic with $a = 0.3905nm$). Also, (100)-$LaAlO_3$ substrates (LAO, pseudocubic with $a = 0.3788nm$) were utilized in order to compare the effect of tensile or compressive stress. The substrates were kept at a constant temperature around $710°C$ during the deposition which was carried out at a pressure of $200mTorr$ of flowing oxygen. After deposition, the samples were slowly cooled to room temperature at a pressure of $500Torr$ of oxygen. The deposition rate is $4Hz$ and the energy density is close to $2J/cm^2$. Further details of the targets preparation and the deposition procedure are given elsewhere[17]. The structural study was done by X-Ray diffraction (XRD) using a Seifert XRD 3000P for the $\Theta - 2\Theta$ scans and a X'Pert Phillips for the in-plane measurements (Cu, Kα , λ=0.15406nm). The composition of the film was checked and corresponds to the nominal one in the limit of the accuracy. Direct current resistivity was measured by a four-probe method under magnetic fields up to 7T using a Quantum Design PPMS and magnetization was recorded using a Quantum Design MPMS SQUID magnetometer as a function of the temperature in the range 4-300K.

Fig.1a shows the $\Theta - 2\Theta$ scan for an as-grown film deposited on STO substrate. Two diffraction peaks can be seen corresponding to an out-of-plane parameter of 0.3865nm. These two peaks can be indexed, based on the cubic perovskite, as the $(100)_C$ and the $(200)_C$ reflections. Note that the high intensity and the sharpness of the peaks, reveal a high quality of the growth which is confirmed by the low value ($\approx 0.3°$) of the full-width-at-half-maximum (FWHM) of the ω-scan recorded around the $(002)_C$ (see inset of Fig.1a). Data used to determine the in-plane lattice parameters of LSFO thin film were obtained from asymmetric XRD scans of the STO (202) and (220) reflections. These scans detected the $(202)_C$ and $(220)_C$ of LSFO. The unit cell is found to be tetragonal with $a = 0.3882nm$ and $c = 0.3865nm$. These values are close to the bulk value, referring to the cubic unit cell

($a \approx 0.387nm$)[11,14]. In fact, the out–of-plane lattice parameter decreases slightly and the in-plane lattice parameter increases lightly confirming that the LSFO film is under tensile stress on STO substrate, keeping the volume of the cell almost constant ($58.24\mathring{A}^3$ in the film to be compared with $57.96\mathring{A}^3$ in the corresponding bulk material). Fig.1b shows a Φ-scan obtained around the $(202)_C$ reflection. Four peaks separated from 90°, are visible and correspond to a four-fold symmetry. The sharp peaks at 90° intervals indicate a perfect in-plane alignment with the substrate. Details investigations of the structure and the microstructure are in progress using high resolution electron microscopy and will be published elsewhere. The $\Theta - 2\Theta$ scan for an as-grown film deposited on LAO substrates is presented in Fig.2. As in the case of STO, two diffraction peaks are clearly visible close to those of the substrate, corresponding to an out-of-plane parameter of $0.386nm$. Surprisingly, this value is very close to the one obtained on STO indicating that the strains seem not to play an important role on the structure (or at least on the lattice parameters) of these compounds. Even if lattice parameters are similar for both substrates, the quality of the film are different. This is evidenced by the full width at half-maximum (FWHM) of the ω-scan recorded around the $(002)_C$ (see inset of Fig.2). On LAO, the value is higher ($\approx 0.4°$) on this substrate. The rocking curves measurements characterize informations on the angular distribution of the LSFO crystallites in the film. Thus, the narrow value on STO as compared to LAO, shows that the c-axis parameter of LSFO films on LAO has a spread mosaicity, i.e. there are not perfectly parallel to each others.

We present in Fig.3 the temperature dependencies of the resistivity as well as the magnetization for a LFSO film grown on STO. The resistivity at room temperature is low ($\approx 10^{-4}\Omega.cm$) but it is still about one order of magnitude higher than in the bulk[11]. When the temperature is decreasing, the resistivity is increasing almost gradually with a semiconductorlike behavior. An anomaly around $180K$ is observed and corresponds to the charge-ordered transition T_{CO}. At this temperature, the magnetization shows a cusp which is characteristic of an antiferromagnetic transition. However, at low temperature the magnetization value is still very high but most probably a result of the substrate component.

Different features can be seen from these datas as compared with the single crystals[11]. First, the cusp in magnetization is weaker in the film and second, there is no an abrupt change in resistivity as seen in LSFO single crystals. This is not surprising because the charge-ordering transition is never as pronounced in thin films[16,17], even if the structure shows an ordering at low temperature[17] and this is due to the presence of substrate which does not allowed the change of lattice parameters below the CO transition observed in the bulk. One can also notice that T_{CO} is $20K$ lower than the in the bulk ($200K$) . The first explanation of the decreasing of the T_{CO} is that, it is often difficult to reach the optimized properties in thin films without a complex growth process[18], mostly due to the substrate-induced strain which bends the structure of the film. Another possibility might comes for the oxygen stoechiometry since the volume of the cell of the film is increasing of $0.3\mathring{A}^3$. According to Dann *et al.*, it would correspond to an increase of the Sr content. Equivalently, this would correspond to an increasing of the oxygen[19]. In our LSFO film, the changes of lattice parameter confirm the tensile stress of the film and an increase of the oxygen content led to a decrease of both lattice parameters (in-plane and out-of-plane)[19]. Since in our case, only one parameter is increasing, we think that the oxygen content is not the reason of such a behavior.

Fig.4 shows the $\rho(T)$ without field and with a $7T$ magnetic field for the LSFO film deposited on LAO. We can see that the film displays an insulating behavior characteristic of the CO compound. However, in this LSFO on LAO, we can notice that the film exhibit a small magnetoresistance effect under a $7T$ magnetic field. Moreover, an anomaly around $260K$ with a thermal hysteresis of few kelvins, are observed. These two features correspond to a transition which is, in fact, close and higher to the T_{CO} transition.

These results indicate that the CO state is weaker when deposited on STO rather than on LAO since the T_{CO} is shifted to higher temperature in the LAO case. In others words, the charge-ordered state becomes more stable under compressive strain. Such feature as been observed recently in the case of manganite thin films where the ferromagnetism is enhanced under tensile stress[17,20] (or equivalently the CO state becomes less stable under tensile stress). The charge-ordered state seems to behave in the same way with Mn and Fe

based compounds. Further compositions need to be investigated in the future to confirm theses results.

In conclusion, we have investigated the structural, transport and magnetic properties of $La_{1/3}Sr_{2/3}FeO_3$ thin films grown by the pulsed laser deposition technique. Highly crystallized films were obtained on both substrates $SrTiO_3$ and $LaAlO_3$. We have seen that the out-of-plane lattice parameter is almost independent of the type of strains. The films show an anomaly in $\rho(T)$ and $M(T)$ close to the corresponding charge-ordered transition observed in the bulk material. However, this transition is lower in the case of STO and higher in the case of LAO, as compared to the bulk compound confirming that a charge-oreder state in less stable under tensile stress. We explained these differences by the stress induced by the substrate upon the film.

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Figures Captions:

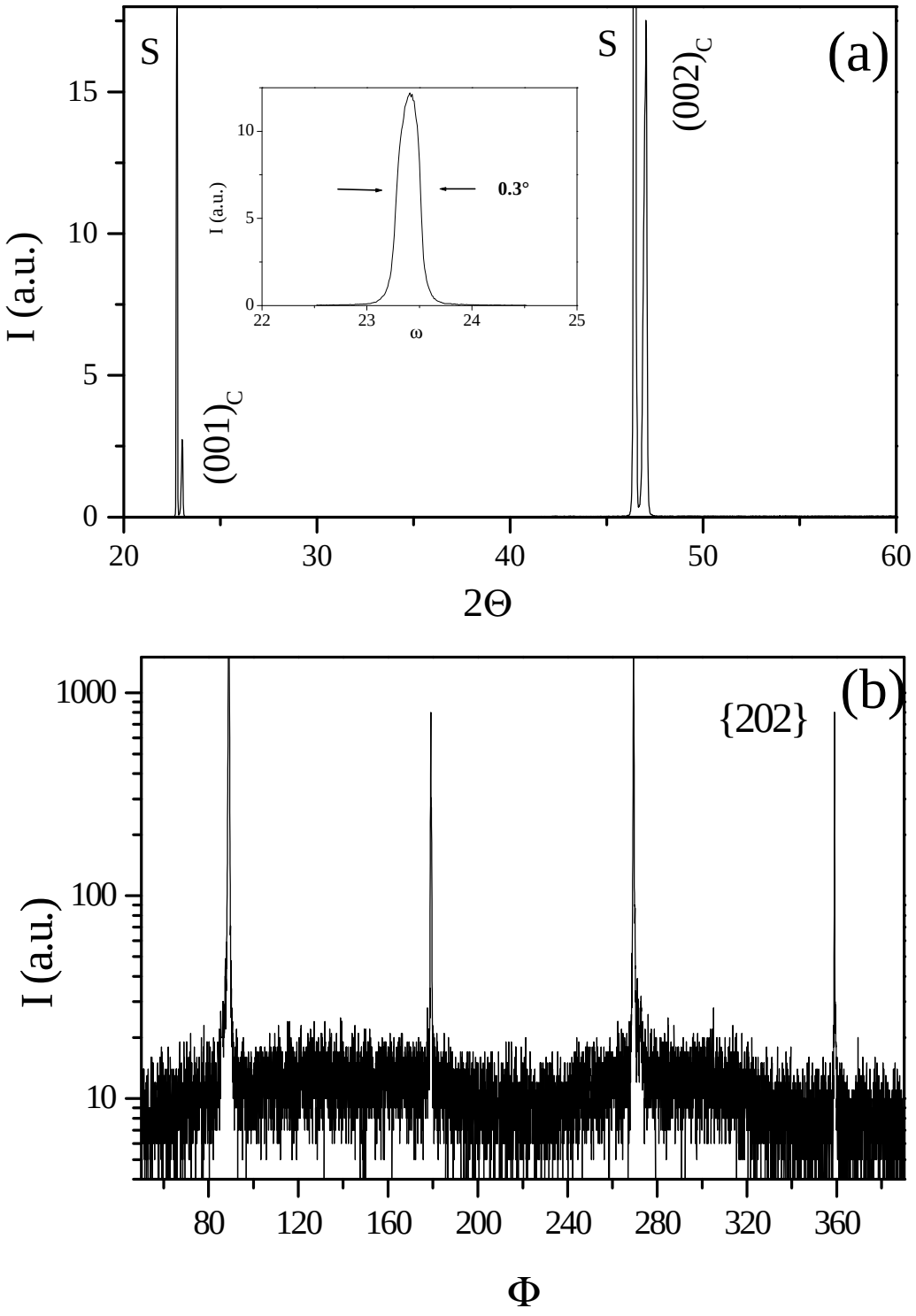
Figure 1a: Room temperature $\Theta - 2\Theta$ XRD pattern of LSFO on STO. Peaks labeled with the index S refer to the substrate peaks. The inset is the rocking curve (ω-scan) of $(002)_C$ reflection of the LSFO film.

Figure 1b: Φ-scan of the $(202)_C$ family peaks in LSFO film showing a very good in-plane orientation of the film.

Figure 2: Room temperature $\Theta - 2\Theta$ XRD pattern of LSFO on LAO. Peaks labeled with the index S refer to the substrate peaks. The inset is the rocking curve (ω-scan) of $(002)_C$ reflection of the LSFO film.

Figure 3: Temperature dependence of the resistivity (ρ) and magnetization (M) at $\mu_0 H = 0.5T$ for a LSFO film on STO. No MR was observed with a 7T magnetic field. The magnetic field is applied perpendicular to the surface of the substrate.

Figure 4: Temperature dependence of the resistivity (ρ) for a LSFO on LAO under different applied magnetic field. Note the small magnetoresistance effect. The inset is magnified resistivity curve in the range $240 - 300K$ showing a clear phase transition around $270K$. The magnetic field is applied perpendicular to the surface of the substrate.



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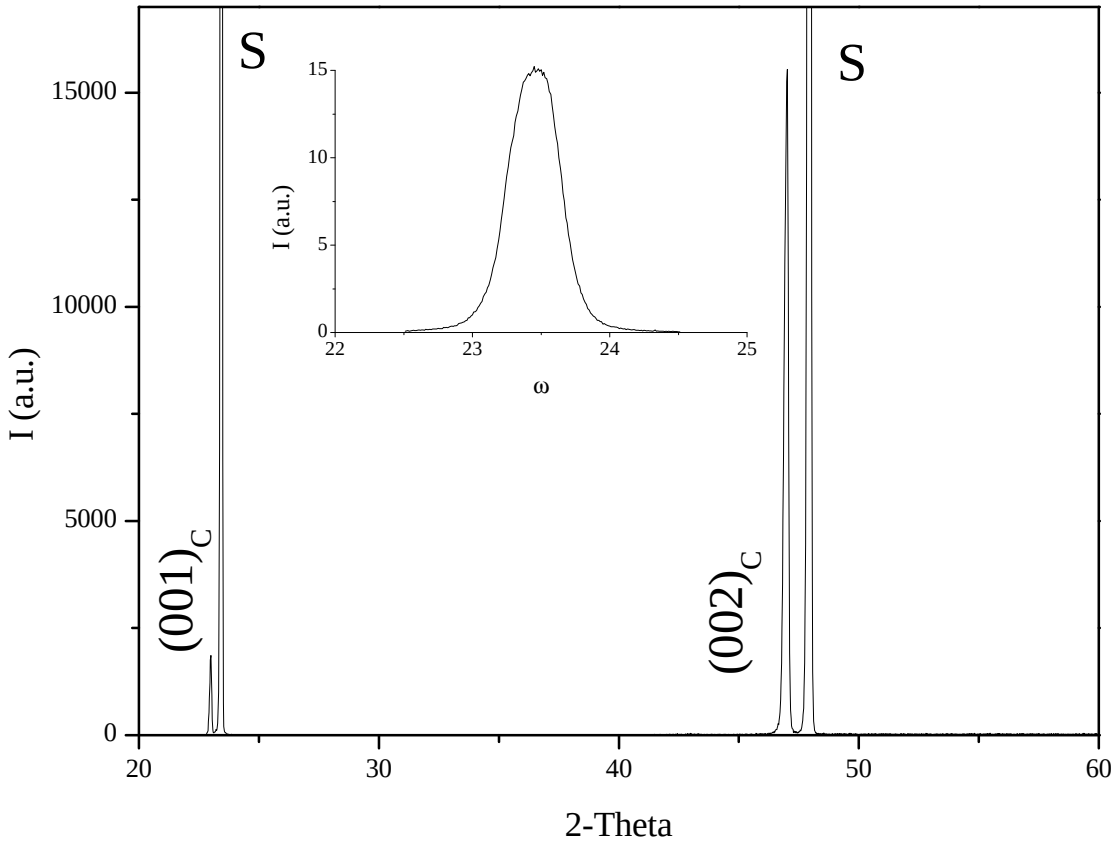

Figure 2

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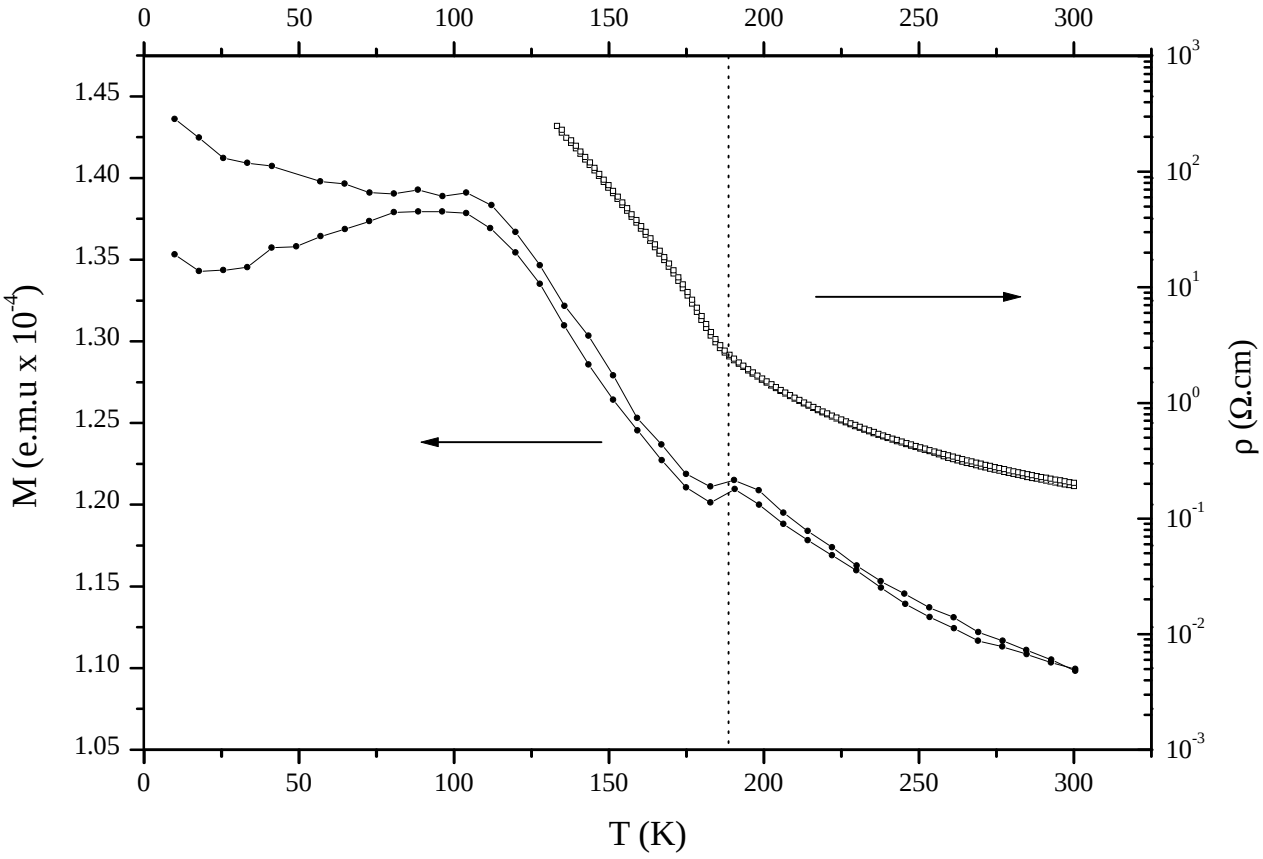

Figure 3

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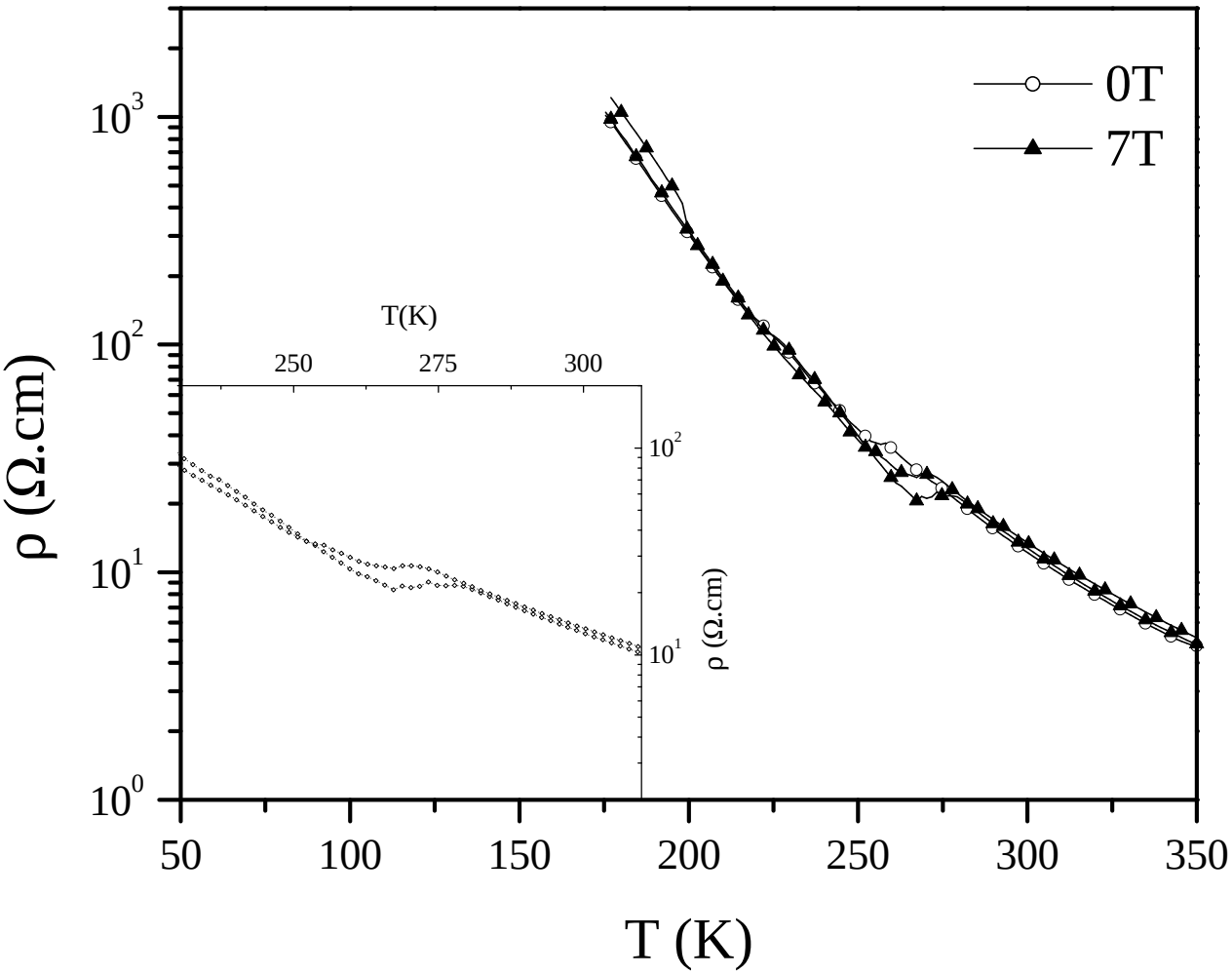

Figure 4

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